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Organic/inorganic-doped aromatic derivative crystals: Growth and properties

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ABSTRACT

Results of a comparative study on the growth from melt by the Bridgman–Stockbarger method of meta-dinitrobenzene (m-DNB) and benzil (Bz) crystals in the same experimental set-up and the same experimental conditions are presented. The incorporation of an inorganic (iodine) dopant in m-DNB was analyzed in the given experimental conditions from the point of view of the solid–liquid interface stability. The limits for a stable growth and the conditions that favor the generation of morphological instability are emphasized. These limits for m-DNB are compatible with those previously determined for Bz, and therefore, even for a high gradient concentration at the growth interface, it is possible to grow m-DNB and Bz crystals in the same experimental conditions characterized by a high ΔT and v. The optical properties were investigated in relation with the dopant incorporation in the crystal in the mentioned experimental conditions. Effects of the dopant (m-DNB/iodine in Bz and iodine in m-DNB) on the optical band gap and optical non-linear properties of the crystals are discussed.

1. Introduction

In the last decades, organic molecular crystals have been considered potential substitutes for inorganic crystals in nonlinear optical applications because they have high values for the nonlinear coefficients, large birefringence values, high damage thresholds in laser beams, and a large transparency domain [1,2]. In the field of nonlinear optical (NLO) phenomena, there is interest in second harmonic generation (SHG) for medical applications and two-photon absorption fluorescence emission (TPF) for potential applications in frequency up conversion lasing, optical power limiting, 3D fluorescence imaging, 3D optical data storage, 3D lithographic micro-fabrication, and photodynamic therapy. Recently, special attention was paid to the study of the synthesis, crystal growth, and characterization of bi-component organic systems for NLO applications [3,4].

Aromatic derivatives are a group of organic compounds that could be interesting for optical nonlinear applications because of the delocalized cloud of π electrons. Meta-dinitrobenzene and benzil are characterized by a large optical band gap and high nonlinear coefficients. These two compounds show different particularities of the chemical structure at the molecular level, but both show important optical nonlinear phenomena.

Meta-dinitrobenzene ($C_6H_4N_2O_4$, m-DNB) is a negative biaxial crystal that belongs to the Pbn21 space group and the point symmetry group mm2. It crystallizes in the orthorhombic system at room temperature and shows good transparency in the range of 0.4–2.5 μm. The crystal has a pyramidal shape with four molecules in the unit cell characterized by the following dimensions: $a=13.20$ Å, $b=13.97$ Å, and $c=3.80$ Å [5]. Diphenyl-α,β-diketone also known as benzil ($C_6H_5COCOC_6H_5$, Bz), is an uniaxial crystal that belongs to the trigonal space group $P3_12_1$ and the point symmetry group D_3^4 $\left(D_3^6\right)$. Good optical quality crystals with a large transparency domain from UV through near IR can be grown. In the benzil unit cell, three molecules are helically disposed and closed packed around the 31 axis, and the hexagonal unit cell dimensions are $a=8.42$ Å and $b=13.75$ Å [6]. There are few studies about the growth from the melt in vertical configuration of m-DNB [3,7,8] and benzil [9–12] crystals but the problem of the growth interface stability was not investigated.

The aim of this paper is to determine the influence of crystal growth conditions on dopant incorporation and the effect of dopant incorporation on the optical properties of pure m-DNB and Bz crystals. We studied two different aspects: (1) the effect of different iodine concentrations ($c=1$ wt% and 2 wt%) on two different matrices, namely m-DNB and Bz; (2) the behavior of

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the same aromatic derivative, m-DNB, as a matrix and a dopant. The systems composed by an aromatic derivative matrix and organic/inorganic dopant have been studied from the point of view of the growth interface stability criterion to analyze dopant incorporation and its effect on the quality of the crystal. We have evaluated the stability limits and the experimental conditions such as the temperature gradient ΔT at the growth interface, and the interface displacement velocity v of the ampoule in the furnace for initiating instabilities. These instabilities could be associated with structural defects and compositional non-homogeneities in the doped crystal of m-DNB. The influence of crystal quality, determined by the particularities of dopant incorporation, on the optical band gap and intensity of the SHG and TPF emissions has been presented for the first time, comparing pure and doped m-DNB and Bz crystals.

2. Experimental

The starting materials provided by Aldrich Inc. (purity 98 wt%) were purified by zone refining in a multiple passages process (between 15 and 25). The m-DNB and Bz crystals were grown by the Bridgman–Stockbarger method. The growth from melt was chosen because both compounds are stable and do not decompose at the melting point. The high purity compounds were introduced into the growth chamber, which was evacuated and sealed under vacuum because the organic compounds show a high affinity for the oxygen and moisture from air. We used the same experimental set-up (Fig. 1a) for both m-DNB ($T_{fusion,m\text{-}DNB}$=89 °C) and Bz ($T_{fusion,BZ}$=95 °C). The thermal profile was determined by the distance between the winding turns of the heater and temperature gradient ΔT by the positioning of the ampoule in the thermal profile. For both the organic compounds, the glass growth chamber (ampoule) had the same geometrical configuration, a conical shape of the tip that is separated by the body of the ampoule through a narrower zone with the purpose of selecting the crystal growth direction [7]. The growth system was adapted to the properties of the organic compounds for the following reasons [1]: (1) the heater has a special thermal profile assuring T_{max}=120 °C, because the compounds have low melting points below 100 °C and steep temperature gradients at the growth interface to counteract the supercooling and initiate crystal growth; (2) the mechanical system assures a low moving speed of the growth chamber to favor the elimination of heat during solidification because of the low thermal conductivity; and (3) the growth chamber has a special geometry to select the growth direction because of the anisotropic growth velocity.

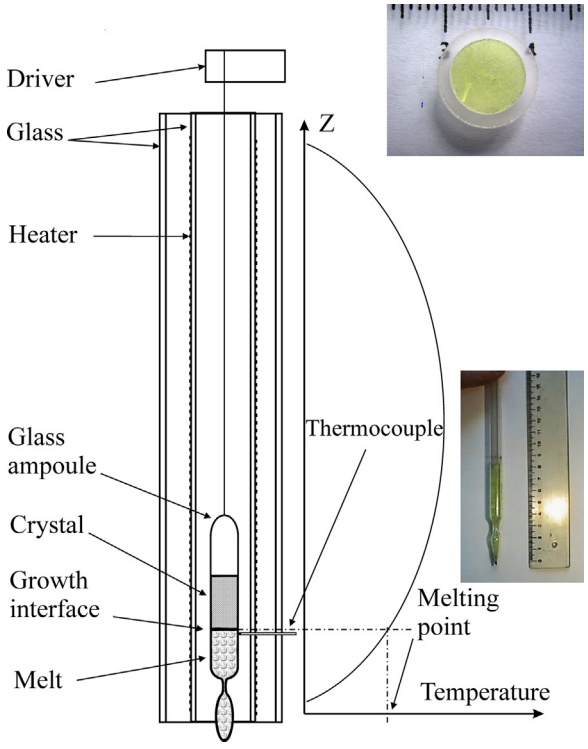

Fig. 1. Experimental set-up for the growth from melt in the Bridgman–Stockbarger configuration of pure and doped m-DNB and benzil crystals. The insets include the image of a typical ampoule containing the ingot of aromatic derivative and the image of a slice cut from this ampoule.

Both pure m-DNB and Bz crystals were grown under the same experimental conditions, ΔT=25 °C/cm and v=1.7 mm/h. To determine the critical values of ΔT and v for the growth of doped m-DNB and Bz crystals, we grew m-DNB crystals doped with 1 and 2 wt% I_2, and Bz crystals doped with 1 wt% I_2 and 3 wt% m-DNB under the same experimental conditions (ΔT=30 °C/cm and v=2.0 mm/h). The growth conditions are slightly different from those for the growth of pure crystals. The final ingots were 65 mm long and 10 mm in diameter. The ingot is not drawn out from the ampoule (Fig. 1). The ampoule containing the benzil or m-DNB crystal is cut with a saw machine with molybdenum wire to obtain slices 2-mm thick (Fig. 1). After this, the glass is mechanically removed and the resulted slices were mechanically polished using a felt tissue on an optically flat glass substrate and a mixture of ethyleneglycol and alumina powder [1,7].

The pictures revealed differences between the slices obtained from pure and doped crystals of benzil (Fig. 2) and pure and doped crystals of m-DNB (Fig. 3).

The X-ray diffraction analysis of pure and doped m-DNB and benzil crystals was performed using powder Bruker D8 Advance Diffractometer with Cu K(α) line, working in locked-coupled mode: V_{acc}=40 kV, I_{anode}=40 mA, increment=0.04°, scan speed 2 sec/step, slit=0.6, scanning range between 10° and 60°. The stage sustaining the sample was rotated about the axis perpendicular to the surface of the slice with a speed of 30 rot/min.

The XRD data are analyzed with TOPAS software package in the Pawley approach to determine the lattice parameters and the indices of the reflection planes. The effect of dopant on the lattice parameters is also analyzed.

The peaks of the diffraction patterns of benzil (Fig. 4a) and m-DNB (Fig. 4b) are attributed using the Powder Diffraction File for benzil (ICDD 30-1539) and m-DNB (ICDD 37-1915). The sharp peaks confirm a good crystallinity of the grown crystals. The crystallographic planes which give stronger reflections are parallel to the slice's surface. The slices were cut perpendicular to the growth direction. The plane giving the strongest reflection in

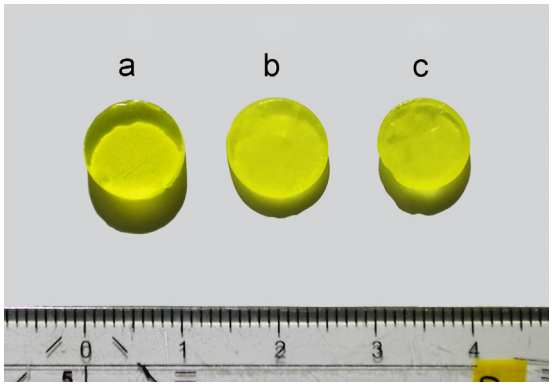

Fig. 2. Typical pictures of benzil slices: (a) pure benzil; (b) benzil doped with m-DNB; and (c) benzil doped with I_2.